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KINETICS OF UNIMOLECULAR DIOXETANONE CHEMILUMINESCENCE. COMPETI--ETC(U)
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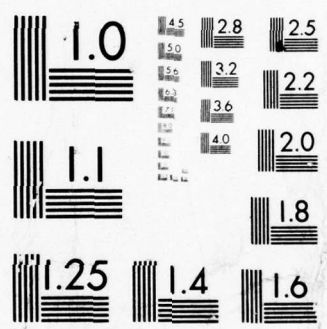
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Kinetics of Unimolecular Dioxetanone Chemiluminescence.

Competitive Parallel Reaction Paths.

by

Gary B. Schuster and Steven P. Schmidt

Prepared for Publication

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School of Chemical Sciences
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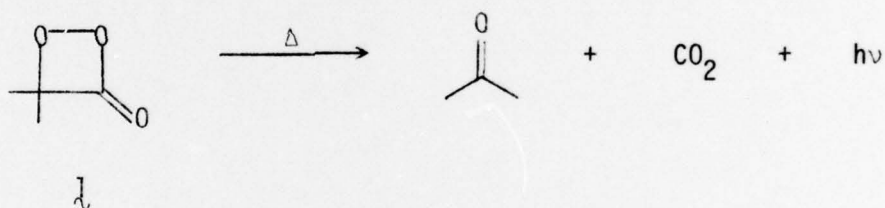
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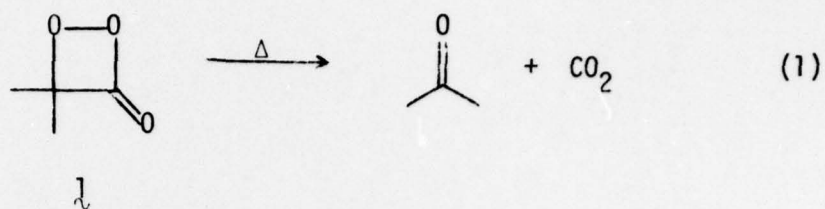
Abstract: Activation parameters and absolute chemiluminescence yields for the thermolysis of dimethyldioxetanone (**1**) were determined. The composite activation energy for the formation of excited singlet acetone was found to be 3-4 kcal/mol greater than the activation energy for the thermal disappearance of **1**. These results are interpreted in terms of two parallel competitive pathways for dioxetanone decomposition, the more highly activated one of which leads to electronically excited acetone.



Kinetics of Unimolecular Dioxetanone Chemiluminescence.
Competitive Parallel Reaction Paths.

Sir:

The thermal unimolecular reaction of the 1,2-dioxetane ring system to generate electronically excited state carbonyl containing compounds is by far the most carefully and extensively studied of all chemiluminescent reactions. The mechanism for this intriguing transformation has been hotly debated by proponents of stepwise and concerted decomposition paths. The ammunition in this controversy ranges from purely theoretical calculations to experimental substituent, solvent, and isotope effects. Of pivotal importance to the dissection of the reaction path have been studies of kinetics and of excited state yields for variously substituted dioxetanes. In a previous report we showed that the major chemiluminescent pathway for dimethyldioxetanone in the presence of an easily oxidized fluorescer is chemically initiated electron exchange luminescence.⁴ In this communication we describe our findings on the uncatalyzed unimolecular thermal fragmentation of dimethyldioxetanone (1) to acetone and CO₂.⁵ This reaction of this remarkable molecule proceeds through at least two distinct experimentally distinguishable transition states. The routing of the reactant through each path and, consequently, the ultimate yield of electronically excited acetone formed, depend critically upon the temperature at which the thermolysis is carried out. These results permit detailed analysis of the reaction coordinate for thermolysis of this system.



The activation energy for the thermal decomposition of **1** was determined by two different techniques in a series of four solvents. First, the total rate of reaction of **1** was measured at several temperatures by monitoring the chemiluminescence decay.⁶ Standard Arrhenius analysis of the decay rate constants gives the activation energies, E_a , shown in Table 1. Second, the activation energy for that fraction of the total reaction that leads to electronically excited singlet states, E_{Chl} , was determined by probing the effect of temperature on the instantaneous chemiluminescence intensity.⁷ Critically, and in contrast to the activation parameters of simply substituted dioxetanes studied thus far, E_{Chl} for **1** is 3-4 kcal/mol greater than E_a , and this difference is independent of the solvent.

The yield of excited state acetone from thermolysis of **1** also demonstrates the unusual effect of temperature. Thermolysis of **1** in $\text{C}_2\text{Cl}_3\text{F}_3$ at 30.0°C generates electronically excited singlet and triplet acetone with efficiencies of 0.1% and 1.5%, respectively.⁸ The singlet excited acetone yield, ϕ_S^* , depends significantly upon the reaction temperature, as is shown in Table 2. These data afford a temperature coefficient for ϕ_S^* of $+4.2 \pm 0.2$ kcal/mol, which represents the difference in activation energies between a higher energy path leading to light generation and the dark decomposition of **1**. This is the first reported example of a temperature dependent singlet excited state yield from the thermal unimolecular reaction of the 1,2-dioxetane ring system.⁹

While trace amounts of catalytic impurities¹⁰ might be expected to induce a parallel dark path of dioxetanone decomposition, and hence result in a lowering of the apparent activation energy, E_a , several experimental observations make such an explanation of our results exceedingly unlikely. Significantly, identical results were obtained for the four solvents, purified by different techniques,¹¹ of Table 1. Thus solvent impurity catalysis would fortuitously have to be equally efficient in all four solvents. Also, the decomposition rate was independent ($\pm 1\%$) of the initial concentration of λ , thereby excluding a possible catalytic impurity in the dioxetanone sample. Furthermore, addition of the chelating agent Na_4EDTA to the reaction mixture had no effect on the observed rate constant. In fact, the powerful catalytic effect of added cupric ion,¹² the metal ion most effective in catalyzing dioxetane decomposition,¹⁰ was completely suppressed by added Na_4EDTA . Finally, the entropy of activation for the thermolysis of λ is -1 ± 3 eu for the four solvents in Table 1. This value is inconsistent with a bimolecular catalysis path, for which a large negative activation entropy would be expected.

The effect of temperature on the efficiency of chemiluminescence from dioxetanone λ is composed of the temperature dependence of the efficiencies of all steps leading to photon generation. The temperature dependence of the fluorescence efficiency of acetone is negligible under these conditions.¹³ Thus, E_{Chl} measures the composite activation energy for the formation of excited singlet acetone. The standard Arrhenius activation energy, E_a , on the other hand, provides a measure of the barrier to the lowest energy transition state available to the system (see below). Our finding that E_{Chl} is 3-4 kcal/mol higher than E_a requires that there be two or more competitive

pathways with discrete transition states for dioxetanone decomposition. The position of these transition states along the reaction coordinate cannot be revealed by this kinetic analysis. Two limiting situations exist, as depicted in Figure 1. In Figure 1a two competitive concerted reactions are represented. In this case the measured difference in activation energy between the light generating and dark paths is equated to the difference in energies between the two transition states. In the mechanism shown in Figure 1b, a common rate determining step leads to generation of an intermediate biradical. This biradical proceeds along a lower energy path to generate ground state acetone and by a more highly activated route to produce singlet excited acetone. The temperature dependence of the instantaneous chemiluminescence intensity for this case is given by eq 2,

$$I = A \exp -(E_a + (E_L - E_D))/RT \quad (2)$$

where A is a constant composed of the preexponential factors and instrument parameters, E_a is the previously defined activation energy for formation of the intermediate biradical, and E_L and E_D are the activation energies for fragmentation of the intermediate to excited and ground state acetone, respectively.¹⁴ Thus, this analysis indicates that the difference in the activation energies between the light generating and non-light generating paths is the difference in transition state energies for the two paths leading from the intermediate biradical.

While our data do not provide a distinction between operation of the two limiting mechanisms depicted in Figure 1, several points warrant discussion. Simple qualitative arguments based upon current theories of pericyclic reactions put forth by Turro and Devaquet¹⁵ predict that for

the concerted path shown in Figure 1a the lower activation energy route should be the one that leads to excited state generation. This prediction is inconsistent with our experimental findings and indicates that either the qualitative model is unreliable or, more likely, that the concerted path is inoperative. On the other hand, the experimentally observed ordering of transition states for both limiting mechanisms depicted in Figure 1 is easily understood in terms of the Hammond postulate in which the most exothermic reaction (formation of ground state products) has the lowest activation barrier. However, neither this line of reasoning, nor any mechanism yet postulated to explain chemical formation of excited states, is capable of explaining why the total yield of acetone excited states from the thermolysis of I is nearly twenty times lower than the excited acetone yield from the less exothermic thermolysis of tetramethyldioxetane.¹⁶ This observation remains a mystery in need of further investigation.

In summary, our investigation of the kinetics of the thermal unimolecular reaction of dioxetanone I has revealed that dual paths are operative. Further experimental resolution of the reaction coordinate is difficult. This reaction may be ideally suited for investigation by ab initio theoretical methods. Such an analysis is planned.

Acknowledgment. This work was supported in part by the Office of Naval Research and in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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- (4) S. P. Schmidt and G. B. Schuster, J. Am. Chem. Soc., 100, 0000 (1978).
- (5) Dimethyldioxetanone (1) was prepared and purified according to the procedure of Adam: W. Adam, A. Alzerreca, J.-C. Liu, and F. Yany, J. Am. Chem. Soc., 99, 5768 (1977).
- (6) Light was detected by the photon counting technique. The disappearance of 1 was strictly first order for at least five half lives over the entire temperature range studied.
- (7) T. Wilson and A. P. Schaap, J. Am. Chem. Soc., 93, 4126 (1971).
- (8) (a) The yield of light was determined by direct comparison with the total integrated acetone fluorescence and phosphorescence intensities from the thermolysis of tetramethyldioxetane (TMD) in $C_2Cl_3F_3$. The yields of singlet and triplet excited acetone from TMD were taken to be 0.2%^{8b,c} and 30%^{8b} respectively. Adam^{8d} has previously reported a singlet excited acetone yield of 0.05% from the thermolysis of 1 at 23°C. His triplet yield, however, is unreliable due to the unexpected involvement, in the presence of rubrene, of an additional

- efficient chemiluminescence mechanism.⁴ A triplet to singlet excitation efficiency ratio of 20 has also been reported previously for I^{8e} and is consistent with our results; (b) T. Wilson, D. E. Golan, M. S. Harris, and A. L. Baumstark, J. Am. Chem. Soc., 98, 1086 (1976); (c) N. J. Turro and P. Lechtken, ibid., 94, 2886 (1972); (d) W. Adam, G. A. Simpson, and F. Yany, J. Phys. Chem., 78, 2559 (1974); (e) N. J. Turro, P. Lechtken, G. Schuster, J. Orell, H.-C. Steinmetzer, J. Am. Chem. Soc., 96, 1627 (1974).
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- (11) Benzene (Burdick and Jackson) and $\text{C}_2\text{Cl}_3\text{F}_3$ (Freon 113, Matheson) were shaken with H_2SO_4 , passed through basic alumina, and distilled. Dichloromethane (Mallinckrodt spectrograde) was distilled from P_2O_5 . Carbon tetrachloride (Mallinckrodt spectrograde) was irradiated (Pyrex) in the presence of benzophenone, passed through basic alumina, and distilled.
- (12) Addition of $\sim 10^{-7}$ M CuCl_2 (with 1% MeOH for solubility) increased the rate of decomposition of I in CH_2Cl_2 by a factor of ~ 10 .
- (13) H.-C. Steinmetzer, A. Yekta, and N. J. Turro, J. Am. Chem. Soc., 96, 282 (1974).
- (14) Invoking the steady state approximation for [Acetone*] leads to eq 3, where, under the experimental conditions, $[\text{I}]$ is constant.⁷ For the case where $k_L \ll k_D$, eq 3 reduces to eq 2 above.

$$I \propto k_A [\text{I}] \frac{k_L}{k_L + k_D} \quad (3)$$

- (15) N. J. Turro and A. Devaquet, J. Am. Chem. Soc., 97, 3859 (1975).
- (16) (a) Calculated values of ΔH_f^0 are: dioxetanone 1, ~ -88 kcal/mol;^{16b} tetramethyldioxetane, -68.8 kcal/mol;^{16c} (b) W. H. Richardson and H. E. O'Neal, J. Am. Chem. Soc., 94, 8665 (1972); (c) W. H. Richardson and H. E. O'Neal, ibid., 92, 6553 (1970).
- (17) Fellow of the Alfred P. Sloan Foundation, 1977-79.

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Table 1. Activation Parameters for the Thermolysis of
Dioxetanone λ .^a

| Solvent | E_a , kcal/mol | E_{Chl} , kcal/mol |
|--------------|------------------|----------------------|
| $C_2Cl_3F_3$ | $22.3 \pm .3^b$ | $25.6 \pm .1$ |
| CCl_4 | $21.3 \pm .3^c$ | $24.5 \pm .5$ |
| PhH | $21.8 \pm .1^c$ | $24.9 \pm .4$ |
| CH_2Cl_2 | $20.8 \pm .1^c$ | $24.8 \pm .4$ |

^aAir saturated solutions, $\sim 5 \times 10^{-4}$ M in λ . ^bEyring activation enthalpy: $\Delta H^\ddagger = 21.7$ kcal/mol; activation entropy, $\Delta S^\ddagger = 0 \pm 1$ eu. ^cSolutions contained 5% Na_4EDTA .

Table 2. Temperature Dependence of the Singlet Excited Acetone Yield from Thermolysis of λ .^a

| Temp., °C | $\phi_S^* \times 10^4$ | Temp., °C | $\phi_S^* \times 10^4$ |
|-----------|------------------------|-----------|------------------------|
| 30.0 | 10 | 9.8 | 5.7 |
| 25.1 | 8.4 | 4.8 | 4.8 |
| 20.5 | 7.4 | 0.3 | 4.5 |
| 15.4 | 6.3 | -5.0 | 3.9 |

^a $C_2Cl_3F_3$ solutions. Yields were determined relative to the yield at 30.0°C. See ref 8a.

Figure Caption

Limiting reaction mechanisms for thermal unimolecular fragmentation of dimethyldioxetanone to acetone and CO_2 . Part A represents the concerted process with two transition states, Part B shows a path proceeding through an intermediate biradical with at least two exit channels.

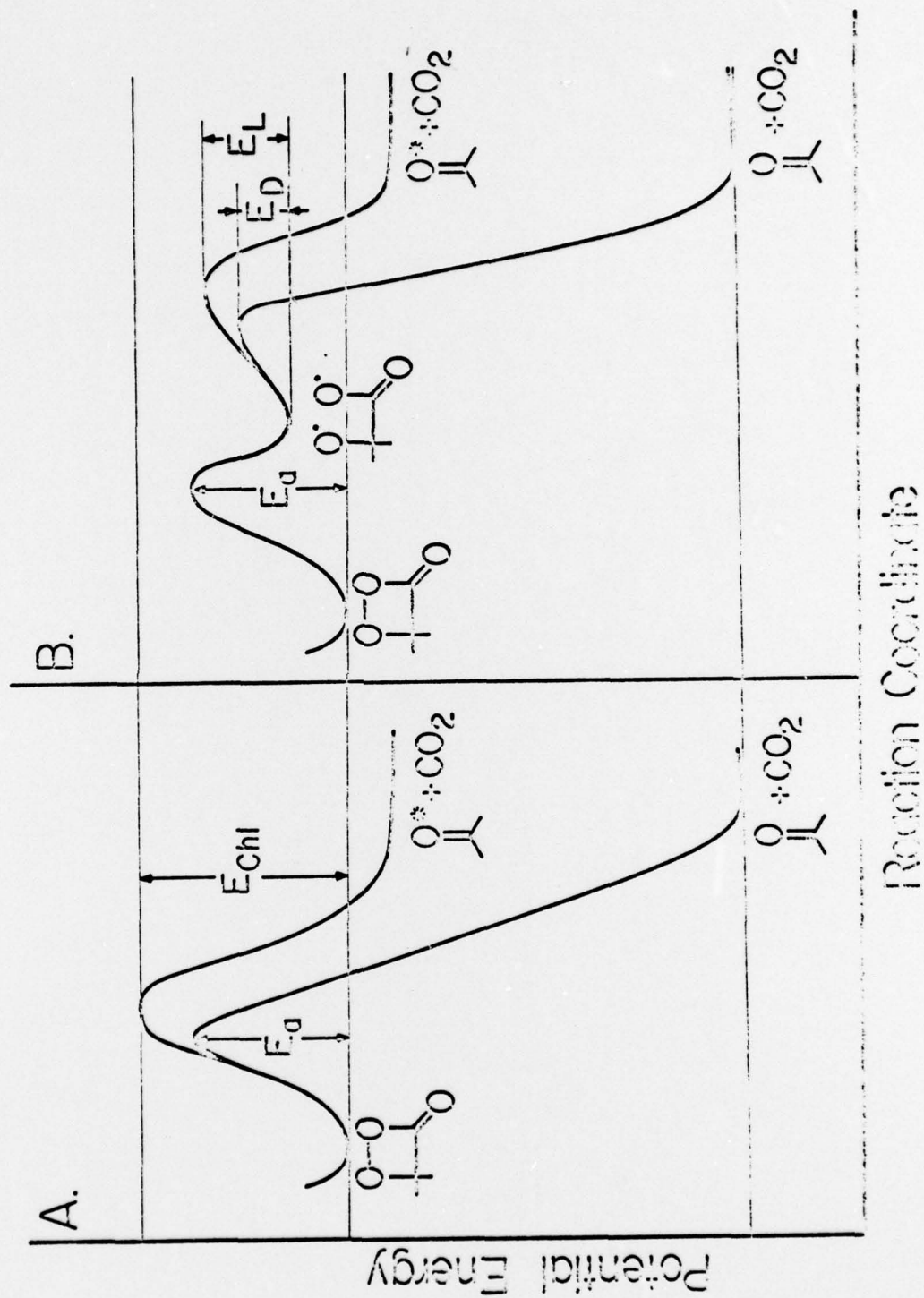


Figure 1.

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